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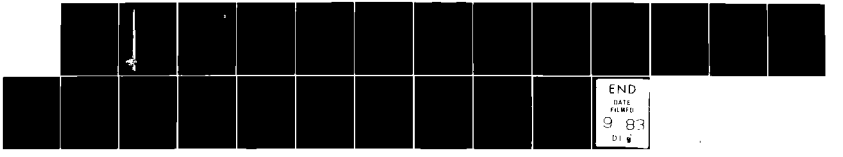

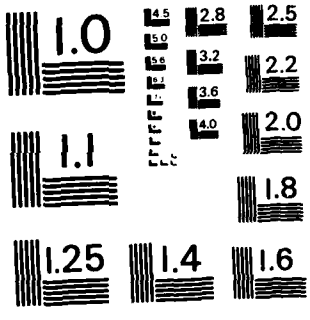

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Report 2380

THE DETERMINATION OF RESEARCH OCTANE NUMBER OF GASOLINE FUELS BY OCTANE ANALYZER

by

Shing-Bong Chen

April 1983

U.S. ARMY MOBILITY EQUIPMENT
RESEARCH AND DEVELOPMENT COMMAND
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Cool Flame	Partial Oxidation
Gasohol	Preignition
Gasoline	Research Octane Number
Motor Octane Number	

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The Foxboro Laboratory Octane Analyzer was investigated as an improved, more reliable, and somewhat less complicated method for assessing octane quality.

The Octane Analyzer's responses (induction time, peak area, and peak height) were correlated with the Research Octane Number (RON), the Motor Octane Number (MON), and the Antiknock Index (RON + MON/2) as determined by ASTM D 2699 and D2700 engine test methods.

Among the three measured responses, peak height was found to give best correlation. In addition, the correla-

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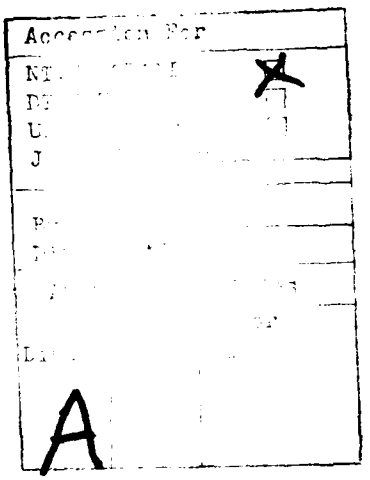
tion was better with the RON and the Antiknock Index than it was with the MON. The Octane numbers of Gasohols and Coordinating Research Council (CRC) full-boiling range unleaded fuels did not correlate with the Analyzer's responses as well as did commercial unleaded gasoline fuels. In conclusion, the Octane Analyzer can be used as a screening test or as an alternate method for measuring the Octane number of gasoline fuels.

CONTENTS



ILLUSTRATIONS

TABLES

THE DETERMINATION OF RESEARCH OCTANE NUMBER OF GASOLINE FUELS BY AN OCTANE ANALYZER

I. INTRODUCTION

The octane number of fuels has been determined, historically, by ASTM-developed engine rating methods. ASTM D 2699 is the procedure used for determining the Research Octane Numbers (RON); ASTM D 2700 is the procedure employed for determining Motor Octane Numbers (MON). Both of these methods require essentially the same engine which is operated under differing conditions for determining either the RON or the MON value. Over the years, difficulties have been associated with the continual maintenance requirements for the Cooperative Fuels Research (CFR) engine, calibration requirements of the engine and detonation-sensing devices, and cooperative testing needed for establishing precision and engine test severity.

Because of the need for an improved, more reliable, and less complicated method for assessing octane quality, the potential for utilizing the Foxboro Laboratory Octane Analyzer was investigated further.

Success with the On-Line Octane Analyzer, developed by the Gulf Research and Development Company[1] and licensed to Foxboro Analytical, has led to an extension of the original design to cover the new Foxboro Areas Model 81-L Laboratory Octane Analyzer. The Model 81-L Analyzer weighs approximately 450 lb and has the dimensions of 24 in. by 24 in. by 41 in. It requires 115 or 220 V a.c. 50 or 60 Hz power, 60 lb/in.^{2} dry clean air, and 100 lb/in.^{2} nitrogen gas.

A Foxboro Model 81-L Octane Analyzer equipped with Areas Microcomputer system was used. The method of analysis which was used simulates the partial oxidation reactions that occur during engine determinations. These reactions are monitored and then correlated with octane ratings. The reactions of interest are precursory to actual combustion and are self-initiating and self-extinguishing. This oxidation reaction is referred to as "cool flames."

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[1] Clinton, R. M. and Puzniak, T. J., "Analyzing Process Octane On-Line," Gulf Research & Development Company Instrumentation Technology (July 1975), pp. 47-50.

The basic measurement consists simply of injecting a small quantity (10 μl) of sample fuel into a flowing air stream and then measuring with a thermocouple the magnitude of the resultant exothermic event after the full-air mixture enters the reaction chamber. The instrument is arranged so that the peak temperature generated during each single reaction is monitored. These peak temperatures have been shown to have good correlation with the research octane number of gasoline fuels, the reaction becoming more severe as the research octane number decreases.

The flow system schematic and analyzer reactor diagram for the Model 81-L are provided as Figures 1 and 2.[2]

II. RESULTS AND DISCUSSIONS

Three Coordinating Research Council (CRC) high-sensitivity, full-boiling-range unleaded reference fuels were used to determine the day-to-day repeatability of the apparatus. The standard deviation and the average results obtained with four runs are shown in Table 1. The measured results are given in Table 2.

Table 1. Standard Deviation (σ) and Average ($\overline{\chi}$) Values at 299.4° C.

RON	Peak Height		Peak Area		Induction Time (min)	
	$\overline{\chi}$	σ	$\overline{\chi}$	σ	$\overline{\chi}$	σ
91.6	2508	35	5.51	0.05	0.53	0.01
96	1026	55	3.91	0.15	0.68	0.01
100	493	25	2.28	0.13	0.89	0.01

In general, the peak height and peak area decreased and induction time increased when the research octane number increased. The peak height and peak area were also increased and the induction time was shorter at higher reactor temperatures compared with lower reactor temperatures. The results obtained during the various runs are discussed as follows:

a. Ron vs Peak Height. The linear plot of Research Octane Number and peak height shows that the peak height gives the best correlation among the three (i.e., peak height, peak area, or induction time) measurement modes for both reactor temperatures used (see Table 3). The plot of peak height (at 303.4° C) vs RON is shown in Figure 3.

[2] "Operation and Maintenance Manual of Laboratory Octane Analyzer," Foxboro Analytical, 1980.

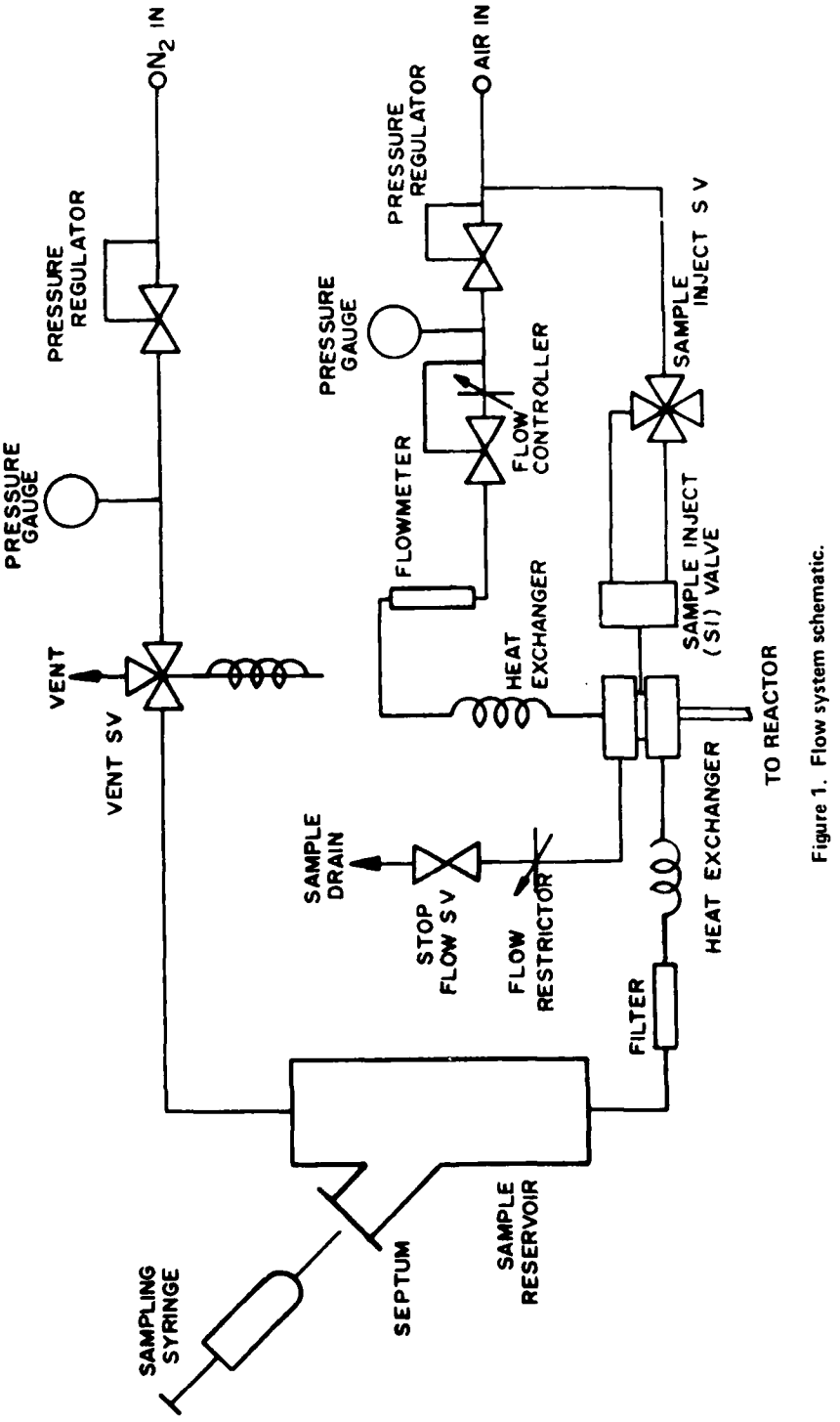

Figure 1. Flow system schematic.

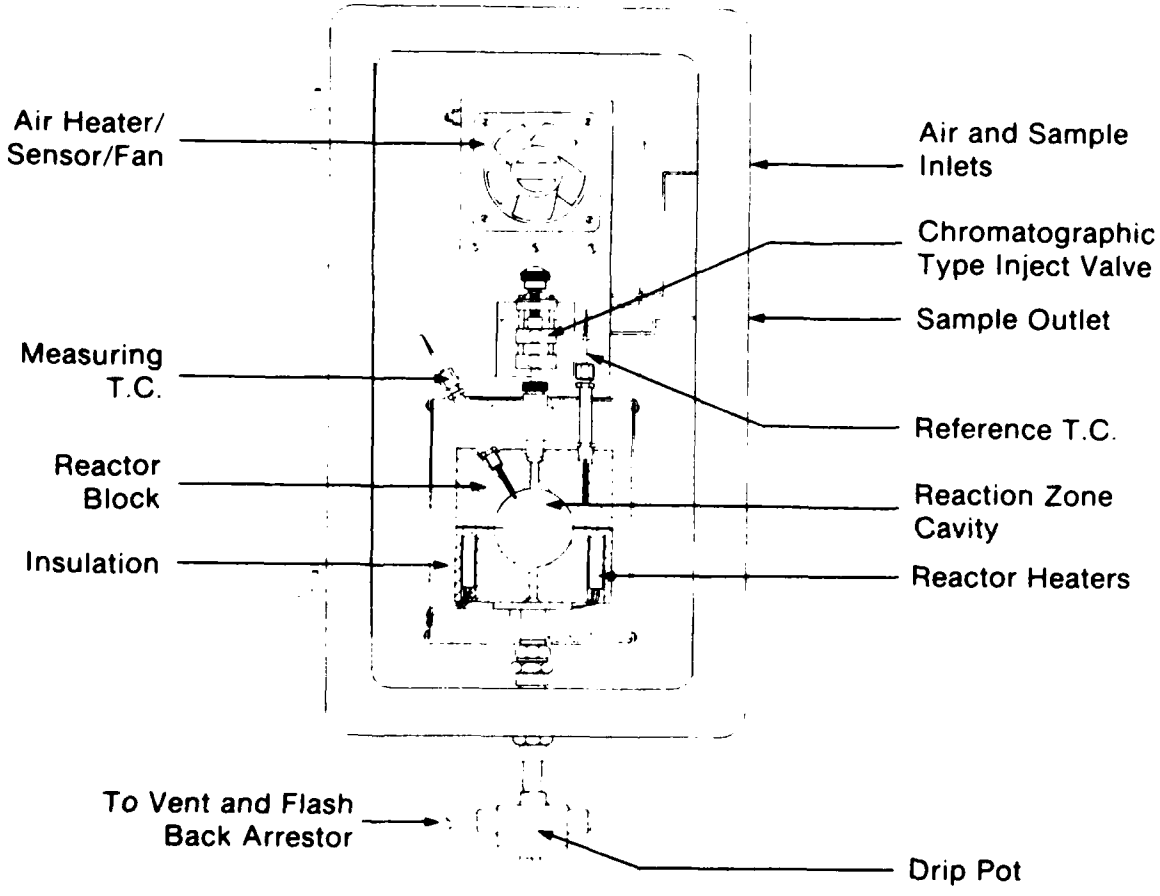

Figure 2. Octane Analyzer Reactor.

Table 2. Measured Results of Gasoline and Gasohol Samples from Octane Analyzer Operated at 299.4°C and 303.4°C

Sample ID	RON	MON	RON + MON / 2	Induction Time (min) @ 299.4°C	Induction Time (min) @ 303.4°C	Peak Area @ 299.4°C	Peak Area @ 303.4°C	Peak Height @ 299.4°C	Peak Height @ 303.4°C
Unleaded Gasoline									
105	96.9	85.0	91.0	0.67	0.58	3.44	4.16	680	969
103	96.5	85.8	91.2	0.53	0.47	4.24	4.64	780	1056
101	96.2	85.6	90.9	0.61	0.52	4.10	4.47	948	1392
102	94.3	85.7	90.0	0.55	0.49	4.70	4.77	1293	1849
470	91.7	82.6	87.2	0.51	0.43	5.27	5.32	1970	2755
478	91.2	83.8	87.5	0.51	0.43	5.15	4.96	2232	2808
473	91.0	83.6	87.3	0.51	0.44	5.40	5.22	2246	2876
480	91.0	82.4	86.7	0.48	0.43	5.31	5.16	3102	3222
475	90.8	83.1	87.0	0.47	0.40	4.86	4.47	2472	2900
Gasohol									
59	98.5	86.0	92.3	0.82	0.77	2.71	2.86	414	462
104	96.2	85.2	90.7	0.73	0.63	2.76	3.46	469	698
191	95.6	84.7	90.2	0.69	0.62	3.97	4.58	817	1036
45	95.5	85.5	90.5	0.67	0.58	4.07	4.56	901	1268
267	94.9	86.7	90.8	0.69	0.59	3.47	4.47	659	1048
257	94.6	86.4	90.5	0.70	0.62	3.48	4.46	625	955
CRC Reference Fuels									
5068	100	87.9	94.0	0.90	0.76	2.24	2.44	475	608
10677	96	84.9	90.5	0.68	0.59	4.07	4.22	1042	1314
5067	91.6	81.7	86.7	0.52	0.45	5.50	5.64	2541	3030
5066	84.4	76.5	80.5	0.42	0.38	6.74	6.80	4042	4015

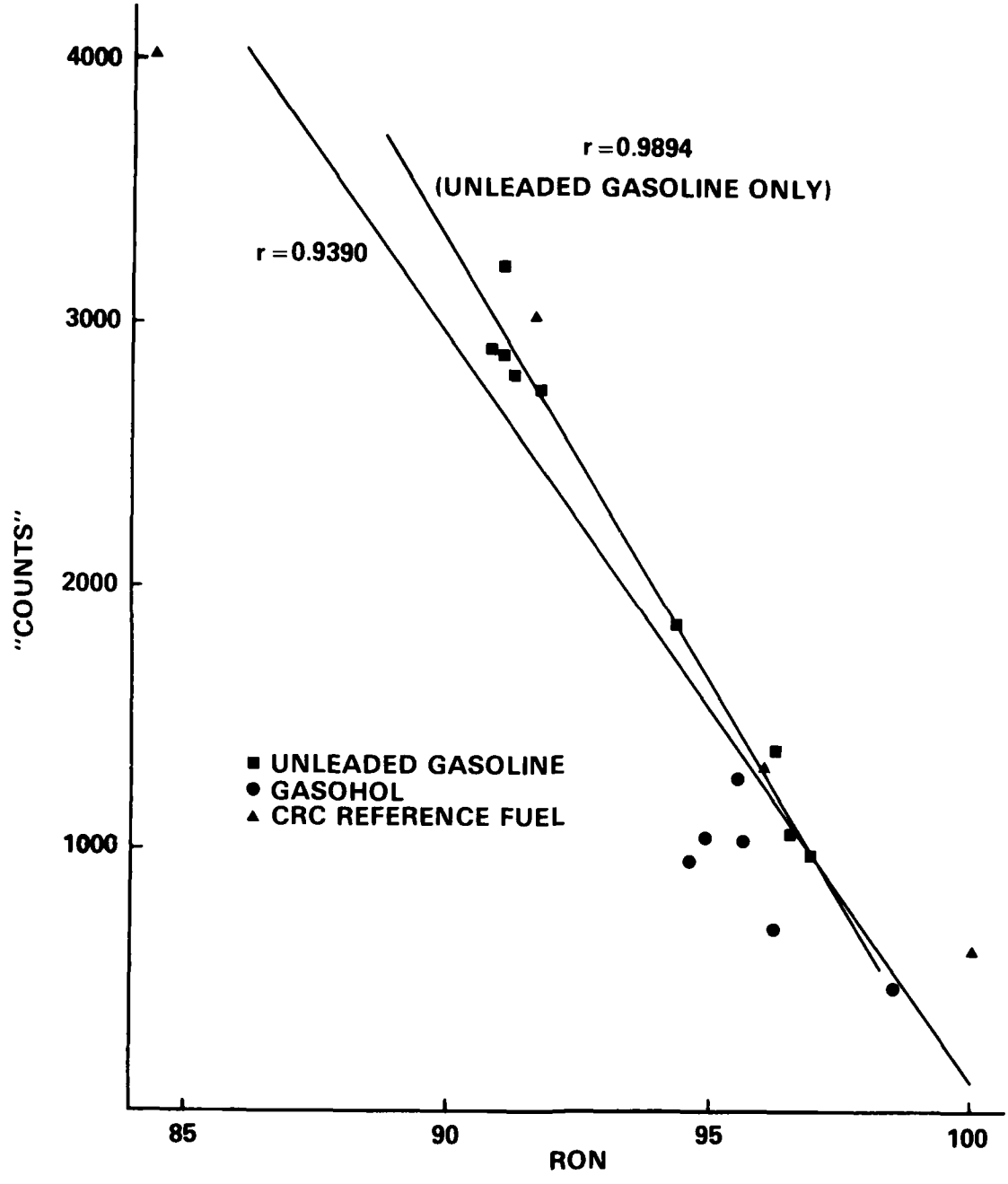

Figure 3. The correlation of RON with relative peak height of Octane Analyzer.

Table 3. The Correlation Coefficients of Octane Number vs Induction Times, Peak Heights, and Peak Areas.

Octane Number	Induction Time @ 299.4 ° C	Induction Time @ 303.4° C	Peak Area @ 299.4° C	Peak Area @ 303.4° C	Peak Area @ 299.4° C	Peak Area @ 303.4° C
RON	0.8574	0.8406	0.9226	0.8905	0.9393	0.9390
MON	0.7471	0.7129	0.8592	0.8212	0.9105	0.8676
$\frac{RON + MON}{2}$	0.8318	0.8075	0.9175	0.8828	0.9480	0.9310

The plot of actual RON (ASTM D 2699) vs estimated RON (obtained from the Octane Analyzer by using the linear calibration curve of nine gasoline fuels as the one in Fig. 3) is shown in Figure 4. Only one sample (RON = 91.0) had a deviation of 0.8 RON. The deviations of the other eight samples ranged from 0.1 to 0.5 RON which falls within the ASTM D 2699 95 percent confidence level of 0.7 RON. Clinton and Puzniak[1] reported that the Analyzer was not sensitive to fuel composition changes resulting from different refining operations such as alkylation, catalytic, cracking, and reforming. However, new refining techniques have been introduced since the issuance of the report which may affect the response factors of the analyzers.

b. RON vs Peak Area. The peak area was thought to be more directly proportional to the released heat which the analyzer monitors. These results, however, did not show better correlation with RON. It can be seen from the typical trace of detector response vs time in Figure 5 that the peaks are not exactly symmetrical and are more asymmetrical in the case of lower RON fuel samples. These data show that peak area measurements *did not give the equivalent* information as with peak height measurements. It is known[2] that changes in temperatures change the linearity of the plot of the primary reference fuel's (iso-octane and heptane mixtures) RON vs Octane Analyzer response. The correlation of RON vs peak area did not show meaningful improvements by changes in the operating temperature of the Octane Analyzer.

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[1] Clinton, R. M. and Puzniak, T. J., "Analyzing Process Octane On-Line," Gulf Research & Development Company Instrumentation Technology (July 1975), pp 47-50.

[2] "Operation and Maintenance Manual of Laboratory Octane Analyzer," Foxboro Analytical, 1980.

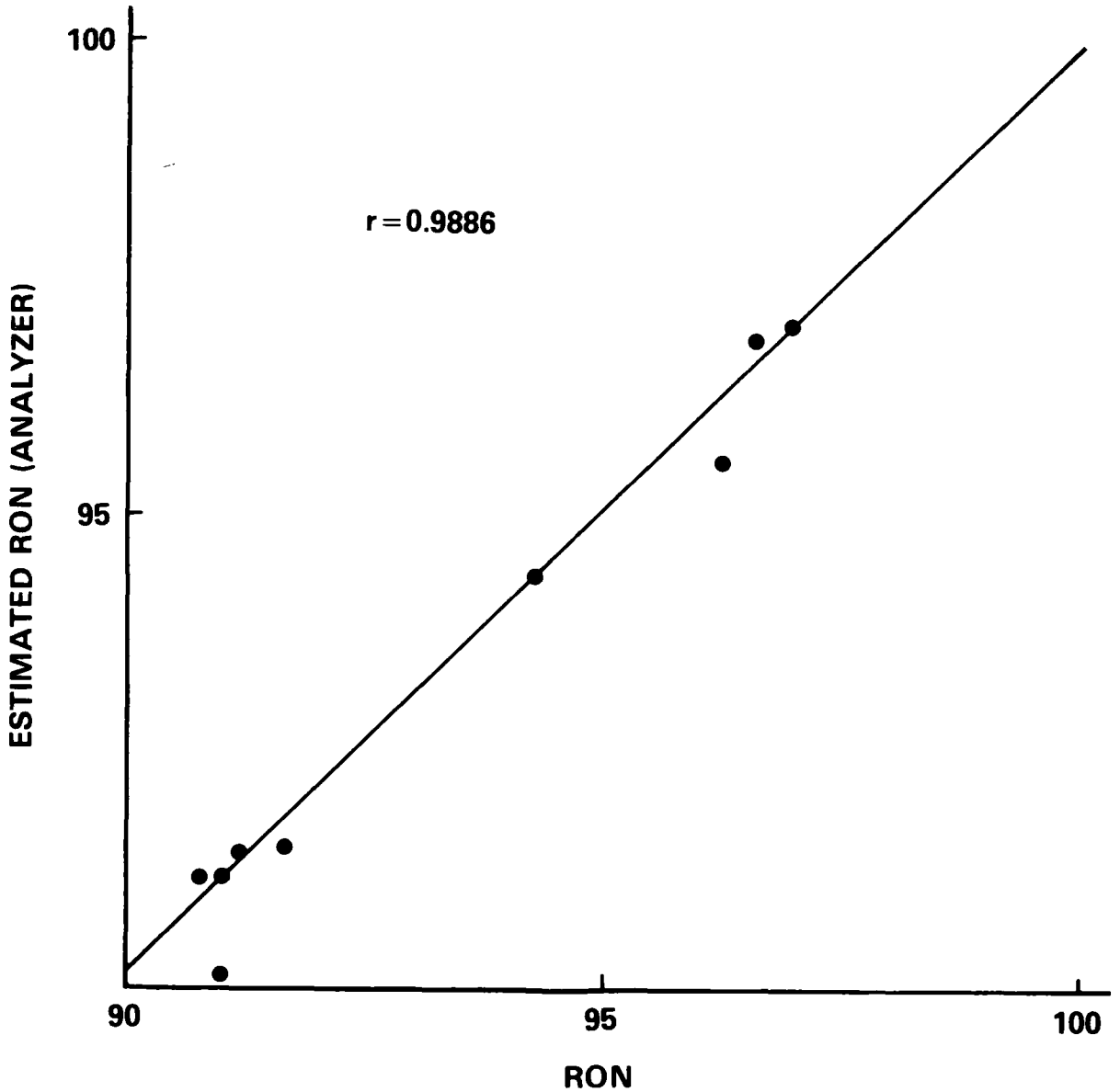

Figure 4. The correlation of RON results between Analyzer and engine test.

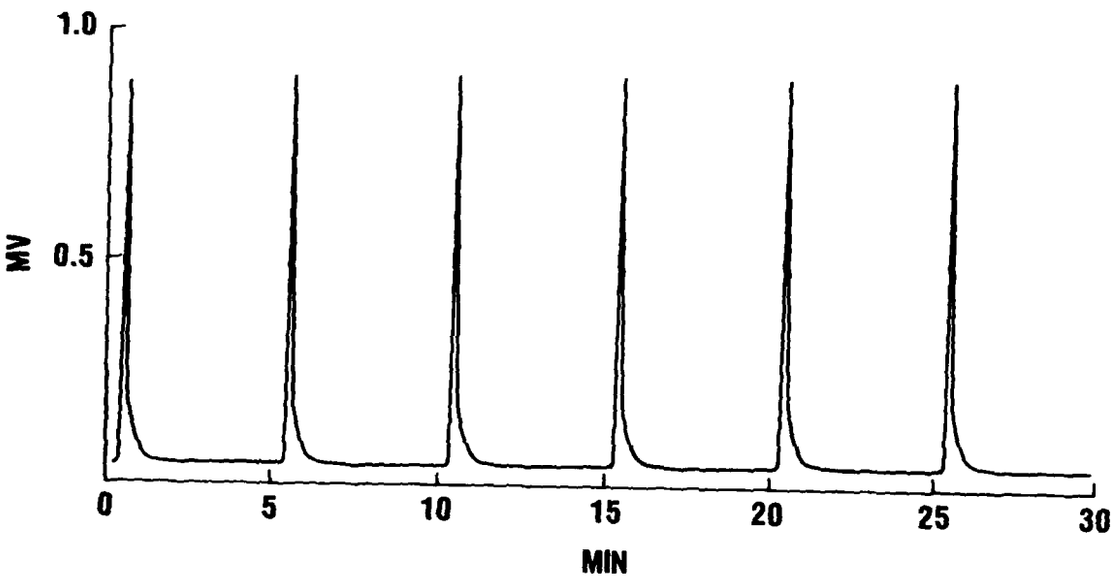

Figure 5. *Thermocouple output* (MV) vs time (min) for gasoline fuel.

c. RON vs Induction Time. Although induction time did not give good correlation vs RON, the five "regular grade" unleaded gasoline samples (90.8 to 91.7 RON) gave shorter induction times than higher RON "premium grade" unleaded and Gasohol fuels.

d. Gasohol and CRC High-Sensitivity Full-Boiling-Range Reference Fuels. Neither Gasohol nor the CRC reference fuels correlated well with unleaded gasolines. The greater differences in fuel compositions probably prohibited good correlation with unleaded gasoline.

e. MON vs Analyzer's Responses. The Analyzer responses (i.e., peak height, peak area, and induction time) were also correlated against motor octane number (MON). However, the correlation coefficient calculation did not show any better here than did those obtained with the RON (see Table 3). It may imply that preignition is less important in the higher speed engine condition in which MON is determined.

f. Antiknock Index (RON + MON/2) vs Analyzer's Responses. The correlation coefficient of antiknock index vs Analyzer's responses was as good as the case of RON (see Table 3). While only commercial unleaded gasoline was used for correlation, the correlation coefficient of antiknock index vs peak height was 0.9872 compared with 0.9894 of RON at 303.4° C reactor temperature.

III. EXPERIMENTS

The basic measurement consists simply of injecting a small quantity (10 μl) of sample fuel from a 10-ml reservoir into a flowing air stream. The magnitude of the resultant exothermic event (e.g., partial oxidation and cool flame reactions) after the fuel-air mixture enters the reaction is monitored by a thermocouple. The instrument is arranged so that the peak temperatures generated during each single reaction are determined and individually recorded. A typical trace detector response versus time for a gasoline sample is shown in Figure 5. A complete analysis consists of six automatically controlled injections at 5-minute intervals. The averages of these measurements (i.e., induction time, peak height, and peak area) are then used for correlation with the Research Octane Number values as determined by ASTM D 2699. Peak temperatures have been shown to exhibit a linear relationship with the RON value of the gasoline. The reaction, however, becomes more severe (e.g., increasing peak temperature) as the RON values decrease.

Because of the limited number of fuels available for this investigation, it was not intended to establish the optimal operation conditions. Two reactor temperatures, 299.4° C and 303.4° C in the range of cool-flame temperature, were chosen. Air flow rate was set at 40 (arbitrary unit) as suggested in the operating manual. The peak heights were obtained from the typewriter terminal. The induction time and peak area were obtained from a Hewlett Packard 3390A Reporting Integrator which was connected to the direct-output terminal on the Octane Analyzer. Both peak height and peak area were measured as relative units. Induction time was measured from the beginning of the automatic process (push start) to the peak of the trace in minutes.

Five samples of regular unleaded gasoline and five Gasohol fuels with known octane ratings were obtained from US Army Fuels and Lubricants Research Laboratory (AFLRL). The fuels and data were obtained courtesy of the Motor Vehicles Manufacturers Association (MVMA). Four "premium" or "super" unleaded gasolines and one Gasohol fuel were collected by AFLRL at local gas stations and rated using the ASTM method.

IV. CONCLUSIONS

The results of this investigative study have generated the following conclusions:

a. The Octane Analyzer could be used to monitor the Research Octane Number (RON) of gasoline fuels. More fuel samples with different RON are needed to define the correlation with engine ratings more accurately. It is necessary to develop a set of three reference fuels for establishing the calibration curve and optimal reaction conditions (e.g., temperature, air flow rate, etc.). This method, if developed, would be suitable for use in the field environment.

b. Antiknock index (RON + MON/2) of gasoline fuel may also be determined by the use of the Octane Analyzer.

c. Fuel composition changes resulting from different refinery processes could possibly affect the Octane Analyzer's response. The sensitivity (RON-MON) of fuel was not found to be a factor for the deviation from correlation line.

d. Gasohol and/or other oxygenated fuels will probably require a different calibration curve with the existing Octane Analyzer.

e. The use of the Octane Analyzer is not intended to replace the existing engine rating method but is an approach to use as a screening test method.

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